

Methane and nitrous oxide fluxes in two coastal wetlands in the northeastern Gulf of Bothnia, Baltic Sea

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Fluxes of CH₄ and N₂O were measured in wetlands in Liminganlahti (Baltic Sea) in the vicinity of the estuaries of the Lumijoki and Temmesjoki. Wetlands were significant sources of CH₄, with a mean flux of 206 mg m⁻² d⁻¹. Methane fluxes correlated positively with temperature and were slightly higher from the wetland of the Lumijoki, where water SO₄²⁻ concentrations were lower. On average, the wetland close to the Temmesjoki was a small source of N₂O (mean flux of 131 µg m⁻² d⁻¹), whereas the wetland close to the Lumijoki was a small sink for N₂O (mean flux of -53 µg m⁻² d⁻¹). The higher availability of nitrogen in the wetland near the Temmesjoki obviously induced the higher N₂O fluxes. Estuarine wetlands seem to be important sources of atmospheric CH₄ but do not represent an important source of N₂O although increased N loading.

Introduction

Estuaries and coastal areas are considered to be significant sources of CH₄ and N₂O, which are important greenhouse gases. Estuarine wetlands offer ideal conditions for greenhouse gas production as they are rich in nitrogen and organic carbon. Both N₂O and CH₄ are produced by heterotrophic microbial processes, which are fuelled by organic carbon. The formation of N₂O is dependent on the availability of nitrogen. In addition to producing gases in estuarine sediments and wetlands, estuaries also release dissolved CH₄ and N₂O transported by rivers to the atmosphere (Jones and Amador 1993, Bange *et al.* 1998). Estuaries and coastal areas are estimated to contribute 35%–60% of all marine N₂O

emissions (Bange *et al.* 1996, Seitzinger *et al.* 2000), while marine ecosystems are estimated to account for 25% of global N₂O emissions (Bouwman *et al.* 1995, Nevison *et al.* 1995). Compared with the N₂O emissions, the contribution of the oceans to global CH₄ emissions is usually considered to be small, only 2% (Cicerone and Oremland 1988), but a great part of that, up to 75%, is emitted from estuaries and coastal areas (Bange *et al.* 1994). Recent studies have shown that estuarine CH₄ emissions may be underestimated (Upstill-Goddard *et al.* 2000) as there is a lack of data and considerable uncertainty about many estuaries around the world.

Estuaries offer ideal environments for the production of CH₄, since they are rich in organic carbon, their hydrologic conditions provide

anoxic conditions, and they have a dense plant system for the transportation of CH_4 from the soil to the atmosphere (Chanton and Whiting 1995, Heyer and Berger 2000). Methane is formed via methanogenesis, which is one of the terminal processes of anaerobic carbon degradation. Production of CH_4 is favoured in environments with a high supply of organic carbon and low content of oxidants, i.e. O_2 , NO_3^- , Mn^{4+} , Fe^{3+} or SO_4^{2-} , which are preferentially used to degrade organic carbon. Rivers transport organic carbon to estuaries, and riverine inputs of nutrients stimulate primary production and carbon degradation in estuarine wetlands (Morris and Bradley 1999). Compared with the oceans, estuaries provide more favourable conditions for methanogenesis, as their SO_4^{2-} concentrations are lower (Capone and Kiene 1988, Upstill-Goddard *et al.* 2000, Middelburg *et al.* 2002). In estuaries the incoming freshwater from rivers dilute saline oceanic water, high in SO_4^{2-} , into brackish water, thus favoring methanogenic activity in estuarine sediments (DeLaune *et al.* 1983). Formed CH_4 is susceptible to oxidation by methanotrophic bacteria if O_2 is present (Hanson and Hanson 1996). In wetlands, oxic and anoxic conditions are controlled mainly through the level of the water table: anoxic degradation is most likely below the water level, whereas aerobic degradation dominates above (Moore and Dalva 1993). The highest oxidation rates occur at the interface of anoxic and oxic zones, where both CH_4 and O_2 are present in high amounts (Hanson and Hanson 1996). Anaerobic oxidation of CH_4 is also possible if enough SO_4^{2-} is present. Anaerobic oxidation of CH_4 has been observed in marine sediments and has been associated with SO_4^{2-} reduction by a consortium of CH_4 -oxidizing archaea and sulphate-reducing bacteria (Boetius *et al.* 2000, Valentine 2002). Plants play an important role in transporting CH_4 in their aerenchyma directly from the anoxic basin to the atmosphere, bypassing the oxidizing zone (Chanton and Whiting 1995). Methane can also bypass the oxidizing zone by ebullition: CH_4 is sparingly soluble in water and forms bubbles when produced in high quantities (Chanton and Whiting 1995).

Estuaries are also potential sources of N_2O , since they are heavily loaded with anthropogenic nitrogen (Kroeze and Seitzinger 1998). Nitrous

oxide is produced in the cycling of N from various microbial processes. In denitrification, N_2O is an intermediate in the reduction of NO_3^- to N_2 (Knowles 1981). Denitrification can either produce or consume N_2O , depending on environmental conditions. N_2O is formed when the last step of denitrification, reduction of N_2O to N_2 , is inhibited, for example by O_2 , NO_3^- , or sulphide (Knowles 1981). In the absence of O_2 and NO_3^- , denitrifying bacteria use N_2O as a terminal electron acceptor, and N_2O is reduced to N_2 resulting in low N_2O release from denitrification (Knowles 1981, Kieseckamp *et al.* 1991). In addition, N_2O is produced as a byproduct from nitrification, where NH_4^+ is oxidized to NO_2^- (Firestone and Davidson 1989) and from dissimilatory reduction of NO_3^- to NH_4^+ (Smith and Zimmerman 1981). Production of N_2O from nitrification is observed at low O_2 concentrations (Firestone and Davidson 1989, de Bie *et al.* 2002). In aquatic sediments, denitrification is the major source of N_2O if NO_3^- is present (Seitzinger 1988), whereas in water columns nitrification has been shown to be a source of N_2O (Rönnner 1983, de Bie *et al.* 2002).

The evaluation of marine greenhouse gas budgets calls for new data from many estuarine ecosystems around the world. Especially the measurements from the northern areas are rare. The shore region of the southern Baltic has previously been shown to be a hot spot for CH_4 , indicating the importance of brackish water ecosystems as a source of CH_4 (Heyer and Berger 2000). There is also a lack of data on N_2O dynamics in the Baltic: previous estimates of Baltic N_2O budgets have been derived from the nitrogen input data, not from real flux measurements (Seitzinger and Kroeze 1998). Here we show the first CH_4 and N_2O flux results from the estuarine wetlands of the northern Baltic Sea and how the gas fluxes are related to water chemistry and physical and biological conditions of wetlands.

Material and methods

Study sites

The coastal marshes studied are a part of the wetland complex of Liminganlahti (64°52'N, 25°21'E, Finland), a bay located in the north-

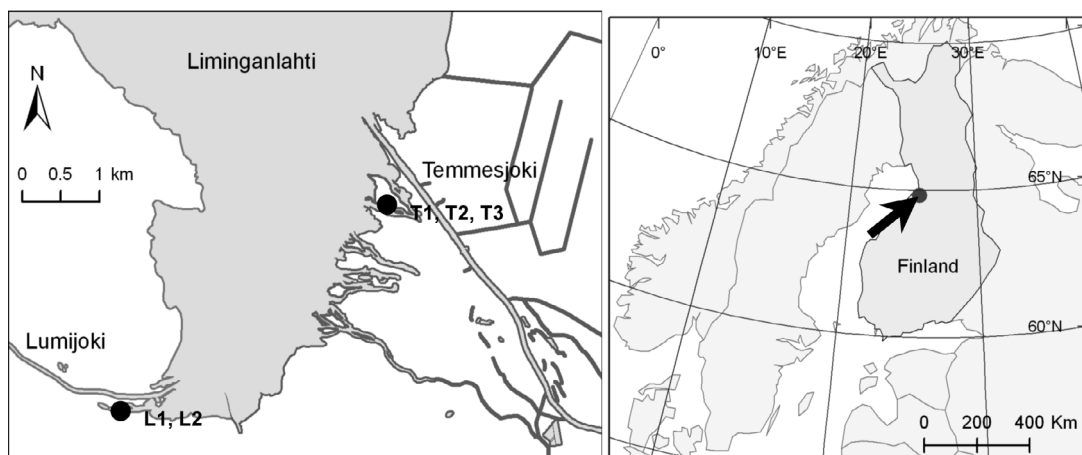


Fig. 1. The location of the study sites in Liminganlahti (Baltic Sea). T1, T2, and T3 are the sub-sites in the wetland of the Temmesjoki; L1 and L2 are the sub-sites in the wetland of the Lumijoki.

eastern part of the Gulf of Bothnia (northern Baltic Sea) (Fig. 1). Liminganlahti that is the largest bay (area 109 km²; shore line length 110 km) within the northern Gulf of Bothnia and has a unique wetland ecosystem. The bay is shallow, with the mean depth of 2.6 m. The sea level and water movements in the bay vary irregularly depending on winds and atmospheric pressure, but tidal changes are negligible. With south and west winds causing high sea levels, water flows from the sea up to the rivers, whereas the reverse occurs with north and east winds that cause low sea levels. Generally north and east winds blow in the spring and early summer and south and west winds become prevailing towards the autumn. Water transportation through the rivers is on average 12 m³ s⁻¹ and 40% of the water in the bay originates from the rivers, thus the water salinity in the bay is less than 1‰ (Kronholm 2005). Therefore, the wetlands of Liminganlahti can be considered as freshwater or brackish wetlands depending on movements of water in the

bay. For more details see Markkola *et al.* (1993).

Wetlands of Liminganlahti were studied in the vicinity of the Temmesjoki (RT) and the Lumijoki (RL). The wetland area of Liminganlahti is about 2400 ha. The main vegetation zones are reeds (1190 ha, 49%), sedges (523 ha, 22%), grasses (303 ha, 13%) and bushes (373 ha, 15%) (Markkola *et al.* 1993). The Temmesjoki and Lumijoki are eupolytrophic and have similar land uses in their catchments: mostly forests (RT = 52%; RL = 49%), agricultural soils (RT = 17%; RL = 15%) and peatlands (RT = 20%; RL = 12%). The rivers and their estuaries have different physical characteristics (Table 1). The Temmesjoki is the largest river entering Liminganlahti: it gathers water from three rivers, with a total catchment area of 1181 km². The Lumijoki is a small river, with a catchment area of 15 km². According to the North Ostrobothnian Environment Centre (Table 1) the Temmesjoki in summer 2004 contained more nitrogen than the Lumijoki, whereas water colour, conductivity

Table 1. Water quality in the Temmesjoki and Lumijoki in summer 2004 (June–August), concentrations of total N (N_{tot}), NH₄⁺-N, NO₂⁻ + NO₃⁻-N, total P (P_{tot}), PO₄²⁻-P, suspended solids (SS), Fe and pH, chemical oxygen demand (COD_{Mn}, oxidation with permanganate), conductivity and colour. Data from the North Ostrobothnian Environment Centre.

	N _{tot} (µg l ⁻¹)	NH ₄ ⁺ -N (µg l ⁻¹)	NO ₂ ⁻ + NO ₃ ⁻ -N (µg l ⁻¹)	P _{tot} (µg l ⁻¹)	PO ₄ ²⁻ -P (µg l ⁻¹)	SS (mg l ⁻¹)	Fe (µg l ⁻¹)	Ph	COD _{Mn} (mg l ⁻¹)	Conductivity (mS m ⁻¹)	Colour (mg Pt l ⁻¹)
Temmesjoki	1620	99	687	84	57	24	4500	6.1	30	24	223
Lumijoki	1130	79	309	91	59	22	8876	6.8	29	15	369

Table 2. Characteristics of the study sites. Dominant species of vegetation were determined at the end of July 2004. Averages and standard errors of the means (in parentheses) of the height of the water table (WT, positive WT indicates the height above the soil surface) and concentrations of NO_3^- , NH_4^+ , SO_4^{2-} and organic acids in wetland water.

Site	Dominant species of vegetation	WT (cm)	NO_3^- ($\mu\text{M NO}_3^-$)	NH_4^+ ($\mu\text{M NH}_4^+$)	SO_4^{2-} ($\mu\text{M SO}_4^{2-}$)	Organic acids ($\mu\text{M C}$)
Wetland of the Temmesjoki						
T1	<i>Carex acuta</i> , <i>Carex aquatilis</i> , <i>Equisetum fluviatile</i>	8.2 (1.1) 15 (2)	8.9 (4.2) 8.0 (5.5)	81 (18) 97 (32)	470 (58) 570 (87)	63 (23) 25 (8)
T2	<i>Carex acuta</i> , <i>Carex aquatilis</i> , <i>Phragmites australis</i> , <i>Equisetum fluviatile</i>	5.9 (1.6)	6.6 (6.3)	98 (46)	390 (120)	61 (50)
T3	<i>Phragmites australis</i> , <i>Carex aquatilis</i>	3.8 (1.8) 7.3 (0.8)	11 (9.7) 0.14 (0.05)	12 (9.7) 42 (10)	430 (100) 170 (36)	100 (50) 52 (15)
Wetland of the Lumijoki						
L1	<i>Carex rostrata</i> , <i>Equisetum palustre</i> , <i>Eleocharis palustris</i> , <i>Carex canescens</i>	11 (1.2)	0.06 (0.01)	37 (8)	200 (59)	49 (21)
L2	<i>Carex nigra</i> , <i>Carex rostrata</i>	3.9 (0.9)	0.22 (0.10)	48 (19)	110 (46)	55 (31)

and content of iron were higher in the Lumijoki. The estuary of the Temmesjoki is located in the middle of the bay and is susceptible to winds, waves, and sea water currents, whereas that of the Lumijoki is smaller and is located in the sheltered part of the bay (Fig. 1).

In this study, we had three sub-sites, T1 (closest to open water) T2, and T3, in the wetland of the Temmesjoki, and two sub-sites, L1 (closest to open water) and L2, in the wetland of the Lumijoki. The sub-sites were located in a transect vertical to the shoreline. The distances between the sites were 30 m and 50 m in the Temmesjoki and the Lumijoki, respectively. The sampling covered two of the most prevailing vegetation zones of the wetlands: the reed and sedge zones. The dominant plant species and the mean height of the water level in the sub-sites are presented in Table 2.

Gas fluxes

Fluxes of CH_4 and N_2O were measured with a static chamber technique (Crill *et al.* 1988), once to twice a week from May to September 2004 (in total 19–22 times per sub-site). Before the measurement period started in May 2004, aluminium collars of 60 cm \times 60 cm were permanently inserted into wetland soil at each sub-site. There were three collars at the sub-sites of the Temmesjoki and four at each sub-site of the Lumijoki. During the measurements, aluminium chambers equipped with battery-operated fans were placed in the water-filled grooves of the collars. Headspace gas samples of 20 ml were collected in polypropylene syringes (Terumo Europe, Leuven, Belgium) equipped with three-way stopcocks (Codan Steritex, Hoejvanger, Denmark) six times during a 30-min incubation period. Gas samples were injected through rubber septa into evacuated vials (12 ml, Labco Exetainer[®], Labco Co., UK). At the time of the measurements, height of the collar above the ground or water surface was measured for determination of the total volume of the measurement chamber (collar and chamber volume).

Concentrations of CH_4 and N_2O in evacuated vials were analyzed within a week in a laboratory with a gas chromatograph (GC) (Agi-

lent 6890N, Agilent Technologies Deutschland GmbH, Waldbronn, Germany) equipped with a peristaltic pump (Minipuls 3, Gilson Inc., Middleton, WI, USA) and an autosampler (Gilson autosampler 222XL, Gilson Inc., Middleton, WI, USA). The GC had two columns (HaysepQ 80/100'' \times 0.9 m and HaysepQ 80/100'' \times 2.7 m), a flame ionization detector (FID) and an electron capture detector (ECD). The temperature of the column oven was 60 °C. After the first column, there was a backflush system, which was switched on when CH₄ and N₂O came through. After the second column, the gases were carried to the detectors, FID for CH₄ and ECD for N₂O. The carrier gas was N₂ with flow of 35 ml min⁻¹. To increase the sensitivity of the ECD, it was also flushed with a 5% CH₄/95% Ar gas mixture (flow = 0.4 ml min⁻¹). The temperatures of the detectors were 200 °C for the FID and 280 °C for the ECD. The GC was controlled and integration was completed with the Chemstation 09.03 program (Agilent Technologies Duetschland GmbH, Waldbronn, Germany). The autosampler and peristaltic pump, which pumped gas samples from the autosampler to the GC, were controlled with the 735 Sampler Software ver. 6.0 (Gilson Inc., Middleton, WI, USA).

The gas fluxes ($\mu\text{g N}_2\text{O m}^{-2} \text{ d}^{-1}$ and $\text{mg CH}_4 \text{ m}^{-2} \text{ d}^{-1}$) were calculated from the change in the mass of CH₄ and N₂O in the chambers over time, using chamber temperature, the collar surface area and the volume of the chamber and the collar space. If the change in the gas concentration was non-linear ($r^2 < 0.9$), the measurement was rejected. However, negligible gas fluxes (for N₂O from -200 to 200 $\mu\text{g m}^{-2} \text{ d}^{-1}$ and for CH₄ from -0.4 to 0.4 $\text{mg m}^{-2} \text{ d}^{-1}$) were included even if their coefficients of determination were < 0.9 . When fluxes are low the concentrations of gases in the chambers do not increase or decrease significantly with time and the coefficient of the determination will be < 0.9 , even though a measurement itself has been successful. These negligible fluxes were taken into account to get a proper distribution of the flux rates.

Environmental variables

At the same time when flux measurements were

carried out, the temperature and the height of the water table (WT) were measured. Temperature was measured from the air, the chamber headspace and the soil at depths of 0, 2, 5, 10, 15, 20 and 30 cm. The height of the WT was measured from the perforated PVC pipes inserted close to the chambers.

The Finnish Institute for Marine Research provided daily means of sea water temperatures and levels from their measurement station in Oulu, located about 20 km north of Liminganlahti. Weather data were monitored at the Oulu airport, which located 8 km north from the estuary of the Temmesjoki. Finavia provided daily means of wind directions and the Finnish Meteorological Institute provided daily means of air temperatures and rainfall.

Wetland water

Concentrations of NO₃⁻, NH₄⁺, SO₄²⁻, and of organic acids (lactate, acetate, propionate, formate and oxalate) in wetland water from each sub-site (one sample from each sub-site) were analysed two to four times a month from June to August. In June, samples were taken from the PVC pipes used in the WT measurements, and in July and August from the PVC pipes placed horizontally in the soil at the depth of 15 cm. The horizontal pipes were inserted into the soil in order to get more representative samples. The pipes were inserted into the soil at the end of June, one week before the first sampling. Ammonium in wetland water was determined photometrically according to Fawcett and Scott (1960). Concentrations of NO₃⁻, SO₄²⁻, and organic acids were determined with the ion chromatographic method developed by Rantakokko *et al.* (2004). Organic acids are produced in the anaerobic degradation of organic matter and are exuded from plant rhizomes (Jones 1998). Organic acids, especially acetate, are precursors and substrates of methanogenesis and they can be used as electron donors (reductants) in denitrification.

Data analysis

Correlation coefficients were determined for

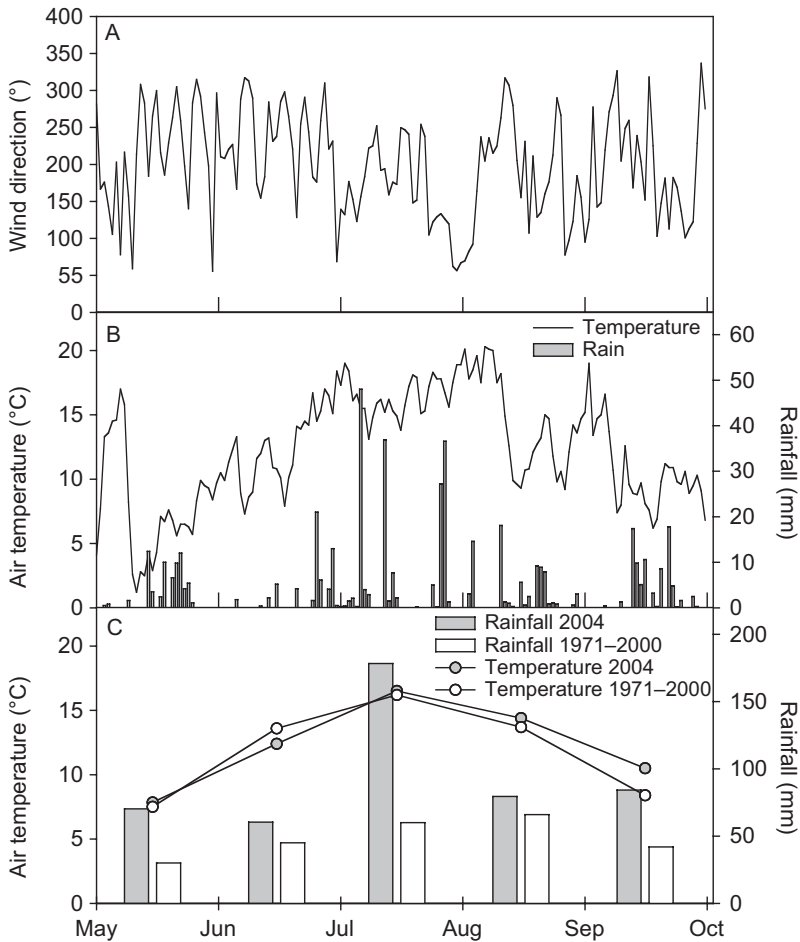


Fig. 2. Weather conditions at the study sites: daily means of (A) wind direction (Finavia), (B) air temperature and rainfall (Finnish Meteorological Institute), and (C) monthly average air temperatures and rainfalls in 2004 and 1971–2000 (Finnish Meteorological Institute).

gas fluxes and environmental conditions (water heights, temperatures and concentrations of nutrients in wetland water). The independent sample *t*-test was used to compare gas fluxes and properties of wetland water between the two sites. The SPSS statistical package (SPSS Inc., Chicago, IL, USA) was used in the statistical analysis.

Results

Environmental characteristics of the sites

During most of the days between May and September (up to 75%), the winds were blowing from south or west (i.e. daily average wind direction was between 135°–315°) (Figs. 1 and 2A). During south and west winds, water gen-

erally flows from the sea up to the rivers; thus during the measurement period the wetlands were greatly affected by water from the sea. The air temperatures were similar to the long-time averages measured in 1971–2000, whereas monthly rainfalls were higher than the long-time averages, especially in July and September (Fig. 2B and C).

Vegetation in both wetlands consisted mostly of sedges (*Carex acuta*, *Carex aquatilis*, *Carex rostrata*, *Carex nigra*) and horsetails (*Equisetum fluviatile* and *Equisetum palustre*) (see Table 2). There were also reeds (*Phragmites australis*) growing at the sub-sites T2 and T3 of the Temmesjoki estuary.

On average, the levels of the water tables were similar in the wetlands (Table 2, Fig. 3A and B). At the sub-sites T1 and L1, which were located closest to open water, the mean water

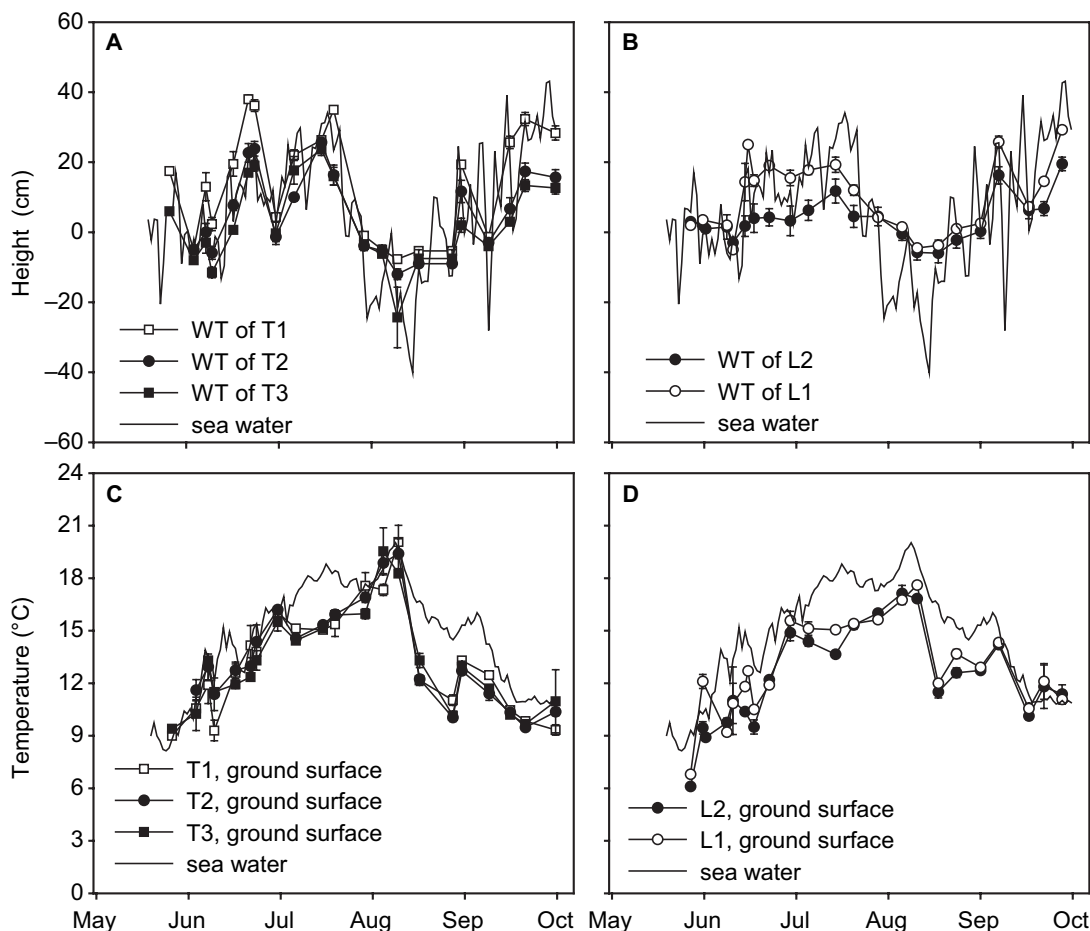


Fig. 3. The temperatures of the sea water (daily means, determined in Oulu) and ground surface (temperature determined in the sub-sites at 0 cm depth at the time of the flux measurements) and hydrological conditions in the wetlands. **(A)** Sea water level and the height of water tables (WT) in the wetland of the Temmesjoki. **(B)** Sea water level and the height of water tables (WT) in the wetland of the Lumijoki. **(C)** Temperature of sea water and ground surface in the wetland of the Temmesjoki. **(D)** Temperature of sea water and ground surface in the wetland of the Lumijoki. Daily means of sea water data were measured in Oulu by the Finnish Institute for Marine Research. For the variables measured in wetlands, averages and standard errors of the means of the 3–4 collars are presented.

levels were 15 and 11 cm, respectively (Table 2). At sub-sites T3 and L2 that were farthest from open water, the mean water level was 4 cm. However, water table fluctuation in the wetland of the Temmesjoki, which was susceptible to waves and sea currents, was more rapid and higher (min WT = –24 cm, max WT = 36 cm) than in the wetland of the Lumijoki (min WT = –6, max WT = 29), which is located in the sheltered part of the bay (Fig. 3A and B). The height of the water table measured in the wetlands and the sea level (Fig. 3A and B) measured in Oulu had a strong positive correlation ($r = 0.786$, p

< 0.001); the correlation was stronger for the Temmesjoki ($r = 0.820$, $p < 0.001$) than for the Lumijoki ($r = 0.751$, $p < 0.001$).

Ground surface temperatures increased from May to August, from 6 °C (sub-site L2 on 27 May) to 22 °C (sub-site T1 on 9 August), and decreased from August to September (Fig. 3C and D). Ground surface and sea water temperatures had a strong positive correlation ($r = 0.826$, $p < 0.001$), and again the correlation was stronger for the Temmesjoki ($r = 0.855$, $p < 0.001$, Fig. 3C) than for the Lumijoki ($r = 0.797$, $p < 0.001$, Fig. 3D).

Wetland water

Concentrations of NO_3^- in wetland water were higher in the wetland of the Temmesjoki than in that of the Lumijoki ($p = 0.047$, Table 2, Fig. 4A and B). In the wetland of the Temmesjoki, NO_3^- concentrations were in general between 0 and $0.8 \mu\text{M}$ NO_3^- , except in the middle of July when higher concentrations, from 45 to $79 \mu\text{M}$ NO_3^- , were detected (Fig. 4A). In the wetland of the Lumijoki, NO_3^- concentrations were generally smaller than $0.13 \mu\text{M}$ NO_3^- , though slightly higher concentrations, up to $1.1 \mu\text{M}$ NO_3^- , were observed at sub-site L2 in August (Fig. 4B). The concentrations of NH_4^+ were on average higher in the wetland of the Temmesjoki than in that of the Lumijoki ($p = 0.047$; Table 1, Fig. 4C and D), but the difference was not statistically significant ($p = 0.075$). In both wetlands, the NH_4^+ concentrations were generally below $100 \mu\text{M}$, though higher concentrations were observed occasionally in July and August (Fig. 4C and D). Sub-site T3 showed significantly lower NH_4^+ concentrations than the other sub-sites (Table 2).

SO_4^{2-} concentrations in the wetland of the Temmesjoki, generally above $200 \mu\text{M}$, were higher than in that of the Lumijoki ($p < 0.001$; Table 2, Fig. 4E and F).

Concentrations of organic acids were similar in both wetlands (Table 2, Fig. 4G and H); generally below $70 \mu\text{M}$ C. Higher concentrations up to $360 \mu\text{M}$ C were detected in August. Organic acid pools were similar in both wetlands: on average 55% acetate, 17% oxalate, 15% formate, 9% propionate and 4% lactate.

Gas fluxes

Both wetlands were significant sources of CH_4 , with a mean CH_4 emission of $206 \text{ mg m}^{-2} \text{ d}^{-1}$ during the measurement period (Table 3). Fluxes of CH_4 were significantly higher from the wetland of the Lumijoki (on average $242 \text{ mg m}^{-2} \text{ d}^{-1}$) than from that of the Temmesjoki (on average $173 \text{ mg m}^{-2} \text{ d}^{-1}$) ($p = 0.008$, Table 3). Within the wetlands, there was no systematic difference in the CH_4 fluxes between the sub-sites, except the considerably lower fluxes from site T3 (Table 3). However, the spatial variation in CH_4 fluxes

was great in the wetland of the Temmesjoki (Fig. 5A). For example, on 30 June fluxes varied from 4.7 to $1820 \text{ mg m}^{-2} \text{ d}^{-1}$ between the sample plots (results from individual sample plots are not shown). The spatial variation was small in the Lumijoki (Fig. 5B). The temporal variation in CH_4 fluxes was also higher and more rapid in the wetland of the Temmesjoki than in the wetland of the Lumijoki (Fig. 5A and B).

In the wetland of the Lumijoki, CH_4 fluxes followed the changes in temperature: ground surface temperature (at 0 cm depth) and CH_4 flux had a strong positive correlation (Table 4). In the wetland of the Temmesjoki, CH_4 emissions also correlated with the ground surface temperature but the correlation was weak (Table 4). CH_4 fluxes had the strongest correlation with soil temperatures at the 5 and 15 cm depths (data not shown): the correlation coefficients were 0.694 and 0.695 in the Lumijoki and 0.469 and 0.462 in the Temmesjoki, respectively ($p < 0.001$ for all coefficients). Water table level and CH_4 fluxes were not strongly correlated (Table 4). The CH_4 fluxes were highest when water level was close to the surface (Fig. 6). In the wetland of the Lumijoki, CH_4 fluxes correlated positively with the total amount of organic acids and concentrations of acetate, oxalate, propionate and formate (Table 4). In the wetland of the Temmesjoki, CH_4 fluxes were not correlated with organic acids.

The wetlands did not emit significant amounts of N_2O ; the mean flux was only $43 \mu\text{g m}^{-2} \text{ d}^{-1}$ (Table 3). In contrast to CH_4 fluxes, N_2O fluxes were significantly greater from the wetland of the Temmesjoki than from the wetland of the Lumijoki ($p < 0.001$, Table 3); while wetland of the Temmesjoki had an average N_2O emission of $131 \mu\text{g m}^{-2} \text{ d}^{-1}$, the wetland of the Lumijoki was a sink of on average $-53 \mu\text{g m}^{-2} \text{ d}^{-1}$. The wetland of the Temmesjoki occasionally emitted significant amounts of N_2O , up to $1421 \mu\text{g m}^{-2} \text{ d}^{-1}$, whereas that of the Lumijoki sometimes acted as a sink, with fluxes of $-1196 \mu\text{g m}^{-2} \text{ d}^{-1}$. In general, both wetlands showed only small fluxes of N_2O : 78% of the fluxes were from -200 to $200 \mu\text{g m}^{-2} \text{ d}^{-1}$ (Fig. 5C and D).

The N_2O fluxes did not correlate with temperatures or water table levels. In the wetland of the Temmesjoki, generally a source of N_2O , the fluxes correlated positively with the total amount

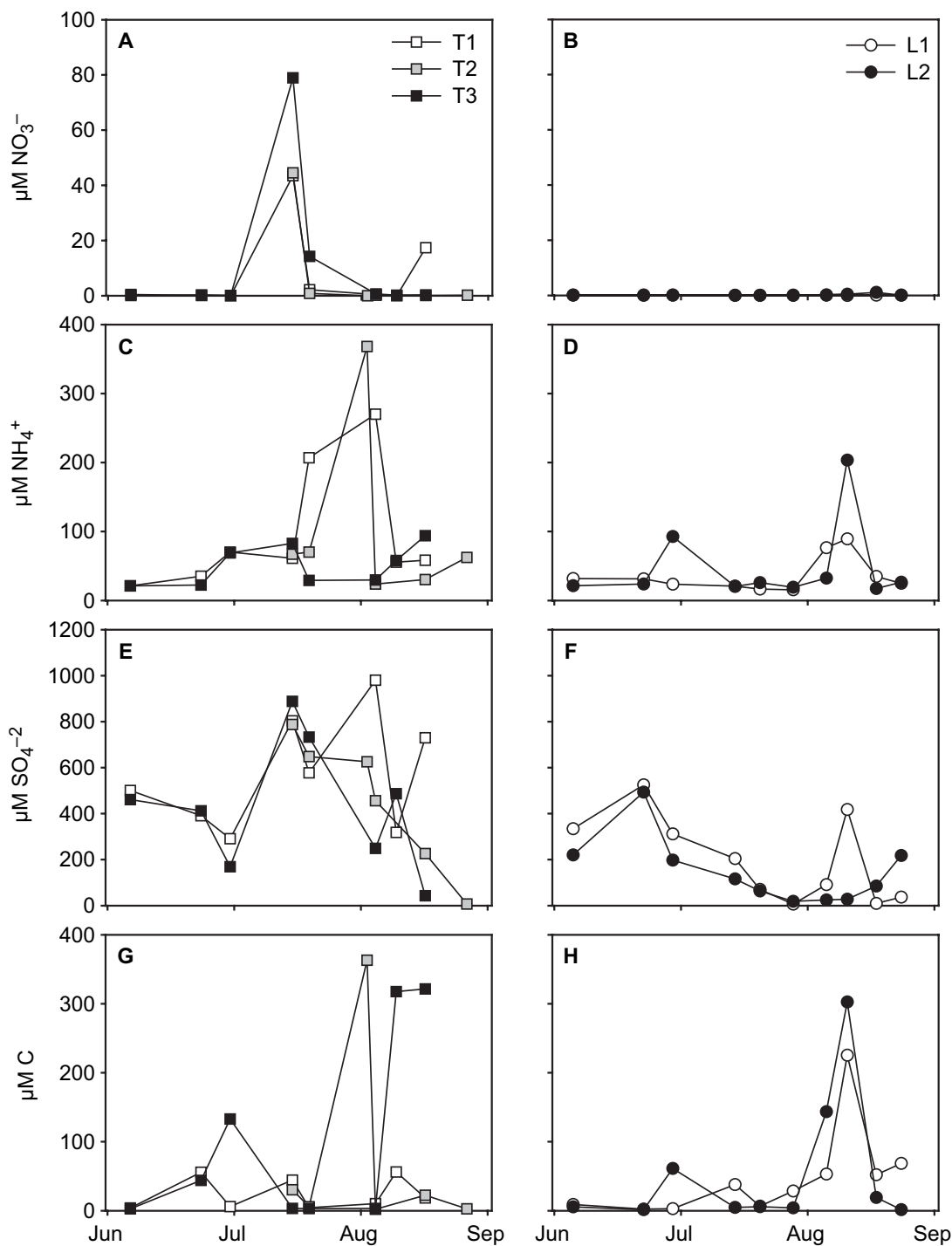


Fig. 4. (A) NO_3^- in the wetland of the Temmesjoki, (B) NO_3^- in the wetland of the Lumijoki, (C) NH_4^+ in the wetland of the Temmesjoki, (D) NH_4^+ in the wetland of the Lumijoki, (E) SO_4^{2-} in the wetland of the Temmesjoki, (F) SO_4^{2-} in the wetland of the Lumijoki, (G) organic acids in the wetland of the Temmesjoki, (H) organic acids in the wetland of the Lumijoki.

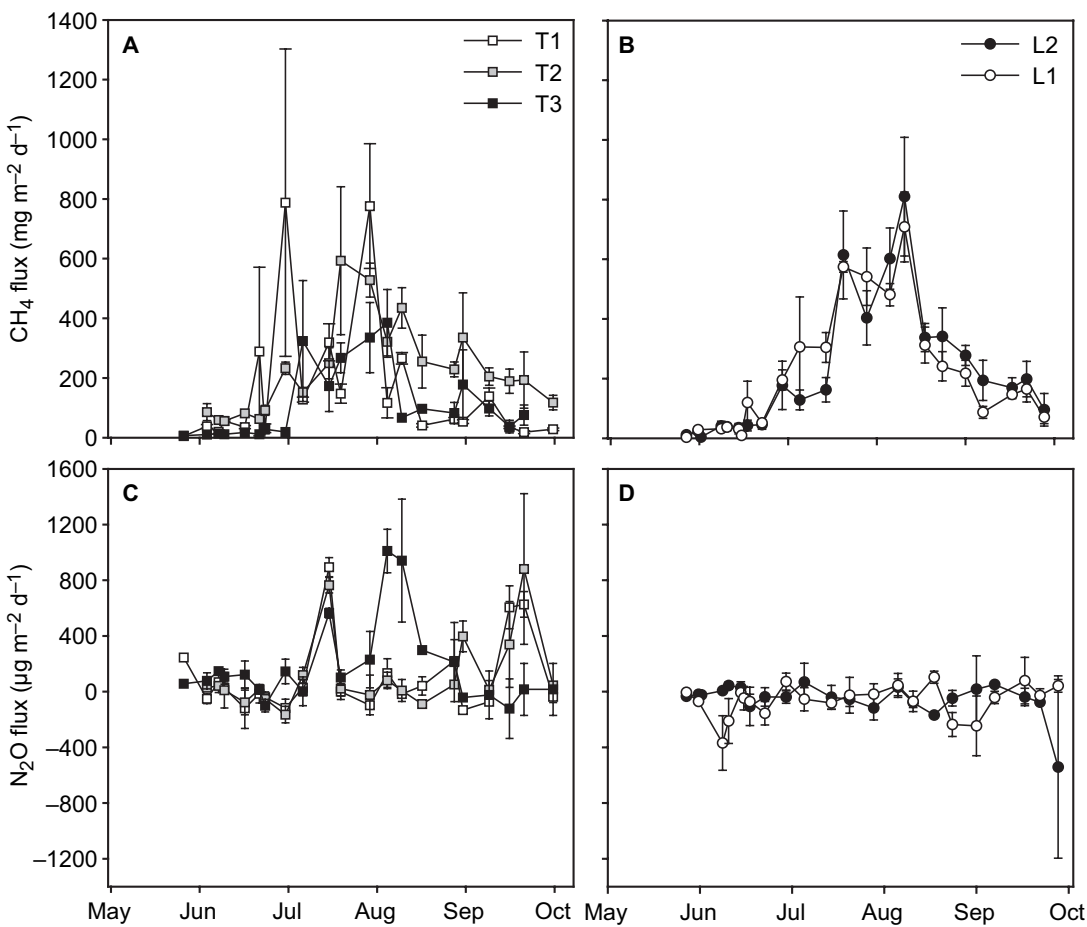


Fig. 5. Fluxes of (A) CH₄ from the wetland of the Temmesjoki, (B) CH₄ from the wetland of the Lumijoki, (C) N₂O from the wetland of the Temmesjoki, (D) N₂O from the wetland of the Lumijoki. Averages and standard errors of the means of the 3–4 collars are presented.

of organic acids and with the concentrations of acetate, oxalate, propionate and formate (Table 4). When the data from both wetlands was ana-

lyzed, the N₂O fluxes correlated positively with the soil water NO₃⁻ concentrations (Table 4).

Table 3. The flux rates of CH₄ and N₂O from the wetlands of the Temmesjoki and Lumijoki and various sub-sites.

Site	CH ₄ flux (mg m ⁻² d ⁻¹)				N ₂ O flux (μg m ⁻² d ⁻¹)			
	Mean	SE	Min.	Max.	Mean	SE	Min.	Max.
All sites	206	13	1.6	1816	43	17	-1196	1421
Temmesjoki	173	17	2.7	1816	131	26	-550	1421
T1	170	40	5.3	1816	117	42	-264	984
T2	223	24	38.0	1062	109	42	-282	1421
T3	118	21	2.7	594	172	53	-550	1382
Lumijoki	242	20	1.6	1232	-53	17	-1196	645
L1	239	26	3.4	971	-62	23	-879	410
L2	245	30	1.6	1232	-43	27	-1196	645

Discussion

Estuarine wetlands as sources of CH₄

The brackish estuarine wetlands are significant sources of CH₄. The average CH₄ emission of 206 mg m⁻² d⁻¹ obtained in this study is within the mean emission range detected from various brackish coastal wetlands around the world (Table 3). Compared with other wetland ecosystems, the brackish water wetlands have intermediate CH₄ emissions: salt marshes have significantly lower rates, whereas freshwater wetlands have similar or higher emissions (Table 5). However, CH₄ emissions seem to be higher from the wetlands of estuaries than from terrestrial wetlands in boreal regions (Table 5). Obviously, a continuous high load of fresh, organic carbon in estuarine wetlands through rivers and from the wetland vegetation together induces high CH₄ production. Emissions of CH₄ generally decrease as salinity increases (DeLaune *et al.* 1983, Bartlett *et al.* 1987, Magenheimer *et al.* 1996). Increasing salinity indicates increasing concentration of SO₄²⁻, which either reduces CH₄ production (Winfrey and Zeikus 1977) or participates in anaerobic oxidation of CH₄ and therefore reduces emissions of CH₄ (Boetius *et al.* 2000, Valentine 2002). Fluxes of CH₄ from brackish estuarine wetlands are much higher than those

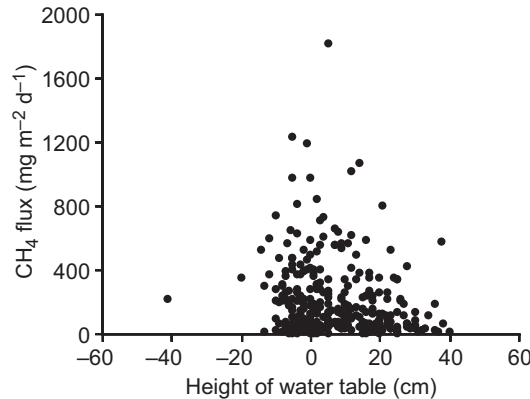


Fig. 6. Flux of CH₄ vs. height of the water table (measurements from the wetlands of the Temmesjoki and the Lumijoki).

from open water areas of estuaries (Table 5). In open water areas, water column CH₄ oxidation can play an important role in limiting the release of CH₄ to the atmosphere (De Angelis and Scranton 1993). Coastal and estuarine CH₄ emissions have usually been quantified only for open water areas from the CH₄ concentration differences between the atmosphere and water with the help of gas transfer velocity (Bange *et al.* 1994, Bange 2006). This method can only be applied for open water areas of the estuaries. However, gas emissions also from estuarine wetlands need to be quantified in order to get reliable greenhouse gas emission estimates for whole estuaries.

Table 4. Correlation coefficients between gas fluxes and environmental variables. *P* values are given in parentheses.

	CH ₄ flux	N ₂ O flux
NO ₂ ⁻ + NO ₃ ⁻ (All sites)	—	0.528 (0.006)
Wetland of the Temmesjoki		
ground surface temperature	0.440 (< 0.001)	—
water table level	- 0.170 (0.032)	—
organic acids (total conc.)	—	0.768 (0.001)
acetate	—	0.771 (0.001)
formate	—	0.760 (0.002)
oxalate	—	0.813 (< 0.001)
propionate	—	0.767 (0.001)
Wetland of the Lumijoki		
ground surface temperature	0.650 (< 0.001)	—
water table level	-0.232 (0.004)	—
organic acids (total conc.)	0.808 (0.001)	—
acetate	0.828 (0.001)	—
formate	0.643 (0.003)	—
oxalate	0.838 (0.001)	—
propionate	0.740 (0.006)	—

Within the Baltic Sea, coastal areas seem to be hot spots for CH₄. Such areas in the southern Baltic Sea (Heyer and Berger 2000) have earlier shown to have high CH₄ emissions. In this study, same was also found for the coastal areas of the northern Baltic Sea. Heyer and Berger (2000) reported CH₄ emissions from 0.3 to 5832 mg m⁻² d⁻¹ in shore regions of the southern Baltic (the mean of the years 1995 and 1996 being 278 mg m⁻² d⁻¹), and we observed emissions from 1.6 to 1816 mg m⁻² d⁻¹ (mean 206 mg m⁻² d⁻¹) in the wetlands of the northern Baltic. The fluxes of CH₄ from open water areas of the Baltic Sea have been orders of magnitude smaller, from -0.007 to 19 mg m⁻² d⁻¹, than those from estuarine wetlands (Bange *et al.* 1994, Bange *et al.* 1998, Bussmann and Suess 1998). Heyer and Berger (2000) suggested that the high CH₄ emissions they detected were induced by the high organic carbon content of the sediments (Heyer and Berger 2000). The temperature regime and

the duration of the measurement periods in our study and in that of Heyer and Berger (2000) were similar, so seasonal variation or temperature were probably not the reasons for the higher CH₄ emissions observed in the southern areas.

The highest fluxes of CH₄ were observed in July and August, when temperatures were highest. It is well known that increasing temperature increases the production of CH₄ in wetlands (King and Wiebe 1978, Christensen *et al.* 2003). The correlation of CH₄ fluxes and temperature was stronger in the wetland of the Lumijoki, located in the sheltered part of the bay. The fluctuations in the water level there were small, which caused less variability in the sediment oxic state. Plant biomass was also highest in July and August (not measured), which may explain the high CH₄ emissions observed.

Plants have an important role in wetland CH₄ dynamics: they deliver organic carbon to sediment methanogenesis, transport CH₄ in their

Table 5. Fluxes of CH₄ from various wetlands. Mean fluxes during the measurement periods of the studies are presented: when a range is given, means from several study sites are included.

Site	CH ₄ emission (mg m ⁻² d ⁻¹)	Source
Saline wetlands		
coastal marsh, Bay of Fundy, Canada	16.3	Magenheimer <i>et al.</i> 1996
coastal marsh, Hudson Bay, Canada	17.8	Moore <i>et al.</i> 1994
coastal tamarack fen, Hudson Bay, Canada	2.2	Moore <i>et al.</i> 1994
coastal marsh, Barataria Basin, Louisiana, USA	15.8	DeLaune <i>et al.</i> 1983
coastal marshes, Sapelo Island, Georgia, USA	1.2–145	King and Wiebe 1978
coastal marsh, Chesapeake Bay, Virginia, USA	15.3	Bartlett <i>et al.</i> 1987
Brackish wetlands		
coastal wetlands, Northern Baltic Sea, Finland	173–242	this study
shallow coastal area, Southern Baltic Sea, Germany	278	Heyer and Berger 2000
coastal marsh, Barataria Basin, Louisiana, USA	267	DeLaune <i>et al.</i> 1983
coastal marsh, Chesapeake Bay, Maryland, USA	43.9	Lipschultz 1981
coastal marshes, Chesapeake Bay, Virginia, USA	50–61	Bartlett <i>et al.</i> 1987
coastal marsh, Florida Bay, USA	642	Burke <i>et al.</i> 1988
coastal lagoon wetland, the West Coast of India	223	Verma <i>et al.</i> 2002
Freshwater wetlands		
littoral wetlands of boreal lakes, Finland	37–107	Juutinen 2004
littoral wetland of a boreal lake, Finland	120	Hyvönen <i>et al.</i> 1998
littoral wetland of a boreal lake, Finland	55–337	Kankaala <i>et al.</i> 2004
marsh, Barataria Basin, Louisiana, USA	588	DeLaune <i>et al.</i> 1983
various marshes, the Mississippi River, Louisiana, USA	251–912	Alford <i>et al.</i> 1997
various marshes, Florida Everglades, USA	29–248	Burke <i>et al.</i> 1988
coastal lagoon wetland, the West Coast of India	4632	Verma <i>et al.</i> 2002
ombrogenous bogs, Finland	124	Nykänen <i>et al.</i> 1998
minerogenous fens, Finland	52	Nykänen <i>et al.</i> 1998
Various European estuaries (open water area)	5.0–10.8	Bange 2006

vascular systems from anoxic sediments directly to the atmosphere, and by transporting O_2 their roots plants can enhance the CH_4 oxidation in the vicinity of their roots (Chanton and Whiting 1995). Plants have two transportation mechanisms for gas transfer: gas molecules either move through plants by diffusion along a concentration gradient or are transported by convective flow. The transportation mechanism is different for various plants; some aquatic species, like *Phragmites australis*, have capability to use convective flow whereas common wetland species like *Carex* spp. use diffusion as a gas ventilation mechanism (Juutinen 2004). In our study the highest CH_4 emissions were observed from the sub-sites where *Carex* species dominated. Site T3, where *Phragmites australis* was dominating, the CH_4 emissions were the lowest. More effective gas transportation mechanism of *Phragmites australis* did not result in higher CH_4 emissions in these wetlands. In addition to transportation, plants also provide substrates for methanogenesis through root exudates and from the degradation of plant and root litter. The content of organic acids indicates the amount of precursors and substrates for methanogenesis. The *Phragmites australis*-dominated sub-site T3 with the lowest CH_4 fluxes had the highest concentrations of organic acids. Site T3 had, on the other hand, the lowest concentrations of NH_4^+ in wetland water (Table 2), which could indicate effective oxidation of NH_4^+ and also CH_4 . Stands of *Phragmites australis* might have resulted in better aeration of the wetland sediments than that of *Carex* species and this could explain the lower CH_4 fluxes observed from site T3.

The variability in CH_4 emissions between the wetland of the Temmesjoki and that of the Lumijoki was probably caused by the different hydrological conditions. The estuary of the Temmesjoki, which is susceptible to winds, waves, and sea water currents, showed great variation in water table levels that reflected in the great temporal and spatial variation in CH_4 emissions. On the other hand, in the more sheltered estuary of the Lumijoki, the CH_4 emissions showed less variation and had a better correlation with temperature and the content of organic acids, substrates of methanogenesis. In general, water level and CH_4 emissions were not strongly correlated. Other

studies have also found that in coastal wetlands and littoral zones of lakes, where the water level fluctuates more rapidly, the correlation between water level and CH_4 emissions is weak (Moore *et al.* 1994, Magenheimer *et al.* 1996). The highest CH_4 emissions have been found when the water level has been, as in our study, close to the sediment surface (Kelley *et al.* 1995, Juutinen 2004). In the case of both low and high water levels, oxidation of CH_4 probably reduces the flux of CH_4 . When the water level falls below the sediment surface, conditions in sediments turn from anoxic to oxic, CH_4 production is inhibited, and CH_4 is oxidized in sediments (Moore and Dalva 1993). However, when the water table is high above the sediment surface, the CH_4 produced in anoxic sediments has to pass through the water column before it is released into the atmosphere. In the oxic water column, dissolved CH_4 is susceptible to oxidation (De Angelis and Scranton 1993, Kelley *et al.* 1995).

Differences in the SO_4^{2-} content between the wetlands might be one reason for the difference in CH_4 emissions. The concentrations of SO_4^{2-} in the wetland of the Lumijoki were on average below 200 μM , but above that value in the wetland of the Temmesjoki (Fig. 4C and D). The inhibitory effect of SO_4^{2-} on methanogenesis has been observed at SO_4^{2-} concentrations of 60–200 μM (Winfrey and Zeikus 1977, Lovley and Klug 1983). Thus, the observed difference in the SO_4^{2-} concentrations between the wetlands is significant for the activity of methanogenic bacteria (Winfrey and Zeikus 1977, Lovley and Klug 1983). However, the inhibitory effect of SO_4^{2-} is affected not only by its concentration but also by the availability of organic carbon (Liikanen *et al.* 2002). Obviously, there has been a large amount of organic carbon in these wetland sediments, since considerable CH_4 production also occurred in the wetland of the Temmesjoki, which generally had SO_4^{2-} concentrations above 200 μM . However, CH_4 emissions in the wetland of the Temmesjoki did not correlate with the concentration of organic acids, which could result from the competition of methanogens and sulphate reducing bacteria for acetate. The SO_4^{2-} concentrations indicate that the wetland of the Lumijoki has mostly been influenced by river water, since SO_4^{2-} concentrations there were

less than 200 μM , which are typical concentrations for freshwater. In contrast, the wetland of the Temmesjoki, with higher SO_4^{2-} content, was obviously influenced by both riverine freshwater and brackish water from the Baltic (Capone and Kiene 1988). During the measurement period, winds were mostly blowing from west and south: during around 75% of the days the prevailing wind direction was between 135° and 315° . West and south winds are known to push water from the sea up to rivers, thus especially to the Temmesjoki, which locates in the bottom of the bay, was obviously greatly influenced by water from the sea.

Estuarine wetlands as sources of N_2O

The estuarine wetlands studied were not significant sources of N_2O : in fact, on average the wetland of the Lumijoki was a sink for atmospheric N_2O . The measured fluxes are similar to those previously measured from saline wetlands, where both small sinks and sources of N_2O have been identified (Table 6). In previous studies, brackish and freshwater wetlands have shown slightly higher N_2O emissions than saline wetlands (Table 6). However, estuarine wetlands seem to have significantly lower N_2O emissions than do open water areas of the estuaries (Table 4). Nitrous oxide emitted from open waters of

estuaries is not all produced *in situ*: a great part of it can be of riverine or terrestrial origin (Bange *et al.* 1998). Another reason for the higher N_2O emissions from open water areas is that oxic water columns provide a better environment for N_2O production than anoxic wetland sediments. In estuaries, significant N_2O production has been observed in the oxic water column via nitrification (Barnes and Owens 1998, de Bie *et al.* 2002), whereas anoxic estuarine sediments have consumed N_2O in denitrification (Middelburg *et al.* 1995).

The availability of inorganic N species controlled the flux of N_2O in the wetlands. The wetland of the Temmesjoki, with higher availabilities of NO_3^- and NH_4^+ , showed higher N_2O fluxes than that of the Lumijoki. When results from both wetlands were analyzed, fluxes of N_2O fluxes correlated positively with the concentrations of NO_3^- . N_2O emission are usually significantly correlated with the availability of NO_3^- (Kieskamp *et al.* 1991). The higher content of NO_3^- in the wetland of the Temmesjoki could be due to the higher riverine loading of NO_3^- or to nitrification in the wetland sediments. The wetland of the Temmesjoki experienced high variation in water level, which caused continuous flooding and draining cycles in sediments. During draining, the sediments become oxic and nitrification can proceed and produce NO_3^- . The NO_3^- produced can be consumed in denitrifica-

Table 6. Fluxes of N_2O from various wetlands. Mean fluxes during the measurement periods of the studies are presented: when a range is given, means from several study sites are included.

Site	N_2O emission ($\mu\text{g m}^{-2} \text{d}^{-1}$)	Source
Saline wetlands		
mud flats, Scheldt estuary, North Sea	-36 to 75	Middelburg <i>et al.</i> 1995
coastal marsh, Barataria Basin, Louisiana, USA	132	Smith <i>et al.</i> 1983
Brackish wetlands		
coastal wetlands, Northern Baltic Sea, Finland	-53 to 131	this study
mud flats, Scheldt estuary, North Sea	385 to 397	Middelburg <i>et al.</i> 1995
coastal marsh, Barataria Basin, Louisiana, USA	204	Smith <i>et al.</i> 1983
Freshwater wetlands		
littoral wetland, a boreal lake, Finland	-151 to 3320	Huttunen <i>et al.</i> 2003
mud flats, Scheldt estuary, North Sea	174 to 609	Middelburg <i>et al.</i> 1995
coastal marsh, Barataria Basin, Louisiana, USA	236	Smith <i>et al.</i> 1983
ombrogenous bogs, Finland	-30 to 5.6	Regina <i>et al.</i> 1996
minerogenous fens, Finland	-26 to 14	Regina <i>et al.</i> 1996
Various European estuaries (open water area)	5380 to 11036	Bange 2006

tion upon flooding of the sediments, when anoxic conditions prevail. Both of these processes, nitrification and denitrification, can produce N_2O . Smith *et al.* (1983) showed that alternate draining and flooding of coastal marsh sediments induced high N_2O emissions. The fluctuating water level could also have promoted the production of N_2O in the wetland of the Temmesjoki.

Also plants might have had an effect on nitrification, denitrification and N_2O fluxes. By providing O_2 to their roots, plants enhance the oxidation of sediments. The sediments at site T3, the only site where *Phragmites australis* was the dominant species of vegetation, probably exhibited better oxidation than the sediments of the other sites. Site T3, showed considerably lower concentrations of NH_4^+ and somewhat higher concentrations of NO_3^- than the other sites indicating effective nitrification, thus providing also more substrates for denitrification (Table 2). Site L2, where the water table was similar to that at site T3 but which was dominated by *Carex* species, had higher NH_4^+ concentrations than site T3. As a result, T3 sub-site showed the highest N_2O emissions among the sub-sites (Table 3).

In the wetland of the Temmesjoki, which was on average a source of N_2O , fluxes of N_2O correlated positively with the concentrations of organic acids, which among other carbon compounds are substrates for denitrifying bacteria. As N_2O correlated positively both with the concentrations of NO_3^- and organic acids, denitrification has probably been an important source of N_2O in this wetland. In the wetlands of the Lumijoki, the shortage of NO_3^- obviously limited denitrification and N_2O production, hence correlation between organic acids and N_2O fluxes was not found.

Representativeness of the study period

The gas fluxes determined here can be used as estimates only for growing season, the period that our flux measurements covered. For example, fluxes of N_2O can be significant during winter and spring when soils go through freezing–thawing cycles (Syväsalö *et al.* 2004). With respect to temperature the measurement period was representative; monthly average temperatures during

the measurement period in 2004 were similar to the long time averages for 1971–2000 (data of the Finnish Meteorological Institute). Because CH_4 emissions had a strong correlation with temperatures, temperature will greatly affect the interannual variation of CH_4 emissions. Monthly rainfall was higher in summer 2004 than the long time averages (data of the Finnish Meteorological Institute). High rainfalls increase river runoff and leaching of nutrients from catchments, especially if the catchments contain lot of agricultural soils. Thus, rivers might have transported more nitrogen and organic matter to the estuarine wetlands in 2004 than in other years. This might have induced higher fluxes of CH_4 and N_2O as the substrate availability increased. Heyer and Berger (2000) observed extremely high interannual variation in coastal CH_4 fluxes in the Baltic: $540 \text{ mg m}^{-2} \text{ d}^{-1}$ in 1995 and $16 \text{ mg m}^{-2} \text{ d}^{-1}$ in 1996. Our results are similar to their average emissions from these two years. Heyer and Berger (2000) evaluated that the observed interannual variability was related to the sediment organic matter content.

Importance of estuarine wetlands greenhouse gas emissions

Estuarine CH_4 emissions have generally been evaluated from CH_4 saturations in surface waters (Bange *et al.* 1994, Upstill-Goddard *et al.* 2000, Middelburg *et al.* 2002, Bange 2006). These estimates have neglected the transition zone between terrestrial and aquatic habitats, i.e. coastal wetlands. However, direct flux measurements made in coastal wetlands (Table 5) show that this area is of great importance for the total estuarine CH_4 budget. Estuarine wetlands have shown systematically higher CH_4 emissions than have open water areas of estuaries (Table 5). Estuarine N_2O emission estimates generally rely on surface water N_2O saturations (Bange *et al.* 1996) or emissions have been extrapolated from nitrogen input data (Seitzinger and Kroeze 1998, Seitzinger *et al.* 2000). Those rare studies which have investigated N_2O dynamics in estuarine wetlands have shown smaller fluxes of N_2O as compared with those from open water areas (Table 6). These very few experiments cannot reveal the

significance of wetlands for coastal N_2O fluxes.

In a boreal landscape, estuarine wetlands are significant sources of CH_4 , average emissions measured from estuarine wetlands of the Baltic have been higher than the averages measured from the littoral wetlands of lakes or from inland bogs and fens (Table 5). Instead, estuarine wetlands seem to be negligible sources of N_2O although increased nitrogen loading to estuaries.

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